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Experimental and Comprehensive Evaluation of Vegetable Oils for Biomass Tar Absorption

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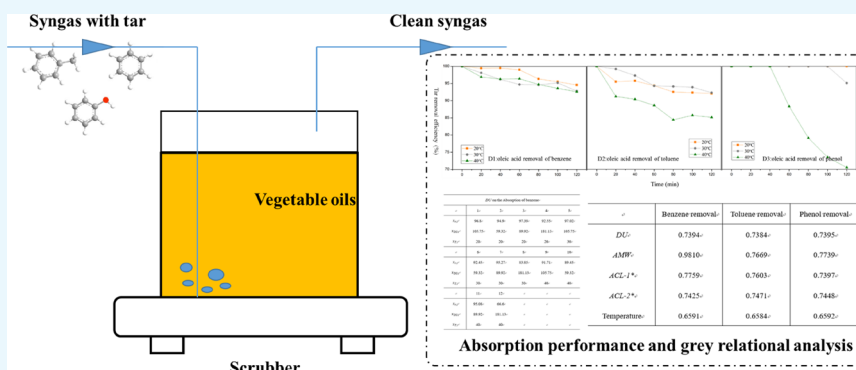
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ABSTRACT: Biomass tar is the bottleneck of biomass gasification, which not only is adverse to energy production but also brings severe environmental issues. A scrubber with vegetable oil is considered as a low-cost but efficient approach for tar removal, but the effects of oil's properties on different tar absorptions were rarely reported. In this study, canola oil, palm oil, and pure oleic acid and linoleic acid, which are the main compounds of vegetable oils, were employed for absorptive removal of benzene, toluene, and phenol. The degree of unsaturation, average molecular weight, and average chain length of solvents were quantitatively characterized. A series of time and temperature-dependent absorption experiments were conducted, and the relationship between oils' properties and absorption performances was built. Results showed that pure oleic acid had the biggest absorption capacity for benzene and toluene due to the mono-unsaturated structure. Increasing the average molecular weight and chain length also enhanced tar absorption. Moreover, Grey relative analysis was employed to investigate the influence of each factor on tar absorption. The average molecular weight exerted the most significant influence on tar absorption in the tested temperature range whose comprehensive relevance coefficients reached the highest at 0.9810, 0.7669, and 0.7739 for benzene, toluene, and phenol, respectively. This study puts more attention on the nature of vegetable oils, and we hope to provide useful information for modulating a better oil-based scrubber medium and further enhancing tar absorptive removal.

1. INTRODUCTION

Biomass, as abundantly available renewable energy,[1] is utilized and developed worldwide under the background of climate alteration and depletion of fossil fuels. Currently, it provides more than 10% of the global energy supply.[2] Gasification is considered as promising technology for the utilization of biomass,[3] which converts biomass into fuel gases, biochar, and useful chemicals.[4] However, tar is inevitably produced during biomass gasification. It plugs the downstream equipment and also decreases the energy efficiency of the entire process.[5] Therefore, the efficient removal of tar is crucial for development and commercialization of biomass gasification.

Generally, tar removal can be classified into two types, mechanical methods and thermal/catalytic methods.[6] Given that a large body of efforts has been given on the research of thermal catalytic processes,[7] these advanced technologies are still facing some obstacles such as intensive energy consumption,[8] the cost of catalysts, and the necessity to modify the gasifiers.[9,10] Therefore, some light has been shed on mechanical tar removal methods. Basically, mechanical methods can be divided into two categories, dry gas cleanups[11] including cyclones, rotating particle separators, filters (fabric and ceramic), and activated carbon absorbers and wet gas cleanups including wet electrostatic precipitators and scrubbers.[12] Distinguished from thermal methods, mechanical methods are usually operated in ambient temperature and thus are safe and energy-saving. Mechanical methods have already been employed at pilot-scale demonstrations and

showed stable removal efficiency as well as economical attractions.[11]

Among which, due to the high adaptability, low construction and operation costs, and relative simplicity, the use of wet scrubbers has proven to be a feasible tar removal method, especially for small-scale gasification.[13] The key issue in this method is the selection of the absorption medium (Table 1).

Table 1. A Brief Summary of Scrubber Media and Corresponding Tar Removal Efficiencies

absorbent	efficiency (%)	references
water	31.8% for gravimetric tar	Phuphuakrat et al.[15]
Pongamia pinnata-based biodiesel	88−92% for real tar derived from a downdraft wood gasifier	Madav et al.[16]
waste cooking oil	81.4% for gravimetric tar	Paethanom et al.[17]
bio-oil	56.8% for heavy tar	Nakamura et al.[18]
bio-oil scrubber combined with char bed	98% by the entire system	Nakamura et al.[22]
vegetable oil	65% to 89% for gravimetric tar	Paethanom et al.[17]
vegetable oil scrubber combined with char absorbent	95% for gravimetric tar	Paethanom et al.[17]

Water was initially investigated, but due to the large proportion of nonpolar[14] hydrophobic components in tar, it showed a poor removal efficiency of only 31.8%.[15] Some hydrophobic oils have been considered, including diesel fuel, which showed a toluene removal efficiency of 95%,[16] waste cooking oil, which achieved 81.4%[17] tar removal, and bio-oil, which provided 56.8%[18] tar removal. However, these media had adverse impacts as their vapors increased the gravimetric tar. The use of high-boiling-point vegetable oils has been suggested for tar removal. Vegetable oils have both nonpolar (fatty acids esterified with glycerol) and polar (carboxyl group) structures, so theoretically, it can trap both hydrophobic and hydrophilic compounds in tar. It was reported that the removal efficiency of a single vegetable oil was in the range of 65% to 89%.[17] Bhoi et al.[19] employed soybean and canola oils as solvents, and it was found that the bed height, temperature, and solvent flow rate exerted significant effects on the model tar removal. Paethanom et al.[17] utilized a vegetable oil scrubber coupled with a char adsorbent for lab-scale tar removal experiments and determined that the efficiency can be higher than 95%. What is more, based on the study of Tarnpradab et al.,[20] the spent vegetable oil could be recovered by filtration and centrifugal sedimentation and the regenerated vegetable oil still showed more than 90% efficiency for gravimetric tar. In one word, vegetable oils, as a low-cost, sustainable, and highly efficient absorber, are the most promising choice for tar removal with scrubbers.[21]

The available studies about vegetable oil-based absorption mostly focused on the mechanical process, such as the formation of microbubbles,[9] the control of bubbler size,[23] and the development of integrated systems,[22] while less attention has been given on the oil itself. Vegetable oils are a general designation of the oily materials derived from vegetables, and they are usually hybrid liquids that contain saturated (cannot chemically add hydrogen) and unsaturated (can be hydrogenated)[24] fatty acids. So which part in vegetable oils is actually responsible for tar removal? Also, what is the determining factor? Up to now, the literature about the effects of oils' properties and compositions on removing different tars is limited. Therefore, in this study, canola oil and palm oil were employed as solvents, and specifically, pure oleic acid and linoleic acid as the main components of vegetable oils were also selected. Deionized water as the polar solvent was employed for comparisons. The compositions of oils were analyzed carefully, and the basic properties, such as the average degree of unsaturation (DU), average chain length (ACL), average molecular weight (AMW) were quantitatively investigated. A series of time and temperature-dependent absorption experiments were conducted for different model tar compounds. Moreover, Grey relational analysis was employed in this study. Grey relational analysis is an applicable method to solve the multiple-attribution decision-making problems.[25] It has been successfully applied to evaluate the effects of different factors on biomass combustion[26] and shale oil production.[27] In this study, the relationship between absorption performance and solvents' properties was built and the relevance was evaluated by Grey relational analysis. This study presents a deeper understanding for tar absorption removal, and we hope to provide valuable information for modulating and evaluating oil-based scrubber media.

2. RESULTS AND DISCUSSION

2.1. Characterization of Oils. The detailed compositions of canola oil and palm oil are listed in Table 2, and information of UD, ACL, AMW, and KV for all oily solvents is also presented in Table 2. It can be found that the main component of vegetable oils is fatty acids between C12 to C20. Among which, lauric acid, myristic acid, palmitic acid, stearic acid, and arachidic acid are saturated, while oleic acid (mono-unsaturated), linoleic acid, and linolenic acid (poly-unsaturated) belong to the unsaturated fatty acid group. Due to the different compositions, vegetable oils have different properties. Because of the largest proportion of long-chain unsaturated fatty acid (such as oleic acid (69.1 wt %) and linoleic acid (19.7 wt %)), the canola oil has the highest UD, CL, and AMW, which are 105.75, 17.77, and 278.32, respectively, while its KV is the lowest at 4.38 mm^2/s (40 °C). As for the two pure solvents, linoleic acid shows the higher DU (as 181.13) due to the poly-unsaturated structure, while its *AMW* is lower than of oleic acid.

2.2. Absorption Removal of Model Tar Compounds. The five solvents were employed to remove model tar compounds containing benzene, toluene, and phenol at 20 °C. The outlet concentrations of benzene and toluene and the corresponding removal efficiencies are plotted in Figure 1. It should be noted that, at 20 °C, all of the five solvents could completely remove phenol in the 2 h runs; thus, the investigation of phenol absorption is presented in Section 2.2.3. Generally, deionized water showed the poorest performance for absorption of benzene and toluene (approximately 35%) due to its polar nature, and the absorption was mainly attributed to the condensation. With increasing the reaction time, the absorption of oils decreased slightly. The average tar removal efficiencies are calculated and arranged as follows: for benzene removal, oleic acid ($\overline{X}$ = 97.39%) > canola oil ($\overline{X}$ = 96.80%) > palm oil ($\overline{X}$ = 94.90%) > linoleic oil ($\overline{X}$ = 92.55%) > deionized water ($\overline{X}$ = 38.49%); for toluene removal, oleic acid ($\overline{X}$ = 93.75%) > canola oil ($\overline{X}$ = 93.67%) > palm oil ($\overline{X}$ = 89.43%) > linoleic oil ($\overline{X}$ = 88.17%) > deionized water ($\overline{X}$ =

Table 2. Compositions and Properties of Oils[a]

oil	compositions (wt %)									UD	AMW	ACL	KV[b] (mm²/s)
	lauric acid (C$_{12}$H$_{24}$O$_2$)	myristic acid (C$_{14}$H$_{28}$O$_2$)	palmitic acid (C$_{16}$H$_{32}$O$_2$)	stearic acid (C$_{18}$H$_{36}$O$_2$)	oleic acid (C$_{18}$H$_{34}$O$_2$)	linoleic acid (C$_{18}$H$_{32}$O$_2$)	linolenic acid (C$_{18}$H$_{30}$O$_2$)	arachidic acid (C$_{20}$H$_{40}$O$_2$)	others				
canola oil	2.8	0.8	2.0	2.1	69.1	19.7	2.9	0.6	0	105.75	278.32	17.77	4.38
palm oil	0.9	0.4	37.9	5.3	41.6	11.8	0.2	0.2	1.7	59.32	255.33	16.87	4.61
oleic acid					100					89.92	282.47	18	4.51
linoleic acid						100				181.13	280.46	18	3.65

[a]The compositions of oils were determined by GC–MS. [b]Kinetic viscosity (KV) is a temperature-dependent property,[18] and the KV value (40 °C) of canola, palm oils, pure oleic acid, and pure linoleic acid were obtained from the literature.[28,29]

37.84%). Therefore, pure oleic acid showed the most outstanding performance, and even at the end of the tests, the removal efficiencies are maintained at a high level (around 94% and 92% for benzene and toluene, respectively). It has been reported that, by using recognized Ni-based catalysts, the conversion efficiency by catalytic cracking of toluene could reach 94%, but 900 °C is necessitated,[5,30] while the highest benzene conversion was only 87% by employing various Ni-supported metal oxide catalysts.[31] Hence, compared with the thermal-catalytic methods, the oleic acid absorption showed superior performance. Additionally, the efficiency of tar cracking or reforming typically decreases after long-time operation due to the deactivation of catalysts. Therefore, the absorption by pure oleic acid can be regarded as an excellent tar removal method, which has stable efficiency for different tars and does not require high temperature.

Apart from oleic acid, canola oil also showed good performance and its removal of benzene and toluene is just a little lower than by oleic acid. This could be explained by the high content of oleic acid in canola oil. Therefore, oleic acid might play a vital role for tar absorption. With a less concentration of oleic acid in palm oil, palm oil showed a relatively poor performance. Besides, linoleic oil exerted less influence compared with oleic acid, and the average removal efficiencies for both toluene and benzene all ranked as second last.

As concluded by previous researchers, tar absorption removal mainly relies on the condensation and dissolution.[14] The condensation process is determined by the operation temperature, which is discussed in Section 2.2.3, while the dissolution effect is typically affected by the "like dissolves like" principle,[32] which indicates that polar solutes dissolve in polar solvents and nonpolar solutes dissolve in nonpolar solvents. Polarity states the charge asymmetry of a molecule. It has a strong relationship with the dipole moment, polarizability, and dielectric constants and is also affected by the polar functional group (for example, carboxyl group), chain length (AC-L),[33] and degree of unsaturation (DU). The determination of polarity of tar and vegetable oils is complicated and time-consuming.[34] Moreover, besides the polar effects, physical absorption,[35] especially van der Waals forces,[15] can also promote tar removal; thus, the kinetics viscosity (KV) and average molecular weight (AMW) are also discussed in the following sections.

2.2.1. Effects of the Degree of Unsaturation (DU). The DU, which is indicated by the iodine value, provides useful information about the stability and oxidation of the oily material.[36] DU increases with the carbon–carbon double bonds but decreases with chain length. Among the four oily solvents, pure linoleic acid has the highest DU due to two double bonds existing in this molecule, while palm oil shows the lowest DU because of the high content of saturated fatty acids, such as palmitic acid and stearic acid. The effect of DU on the removal of different model tar compounds is depicted in Figure 2 as well as the corresponding fitting curves. In general, the removal efficiency of benzene is slightly higher than that of toluene, and both of them increase with DU first then decrease sharply. The peaks of the curves appeared at around 110, which is close to the value of canola and oleic oils, while for linoleic acid, which has the highest DU, showed the poorest performance. According to the curves, it implied that, in the low DU range, increasing DU was favorable for tar removal, which can be explained by the enhancement of hydrogen bond
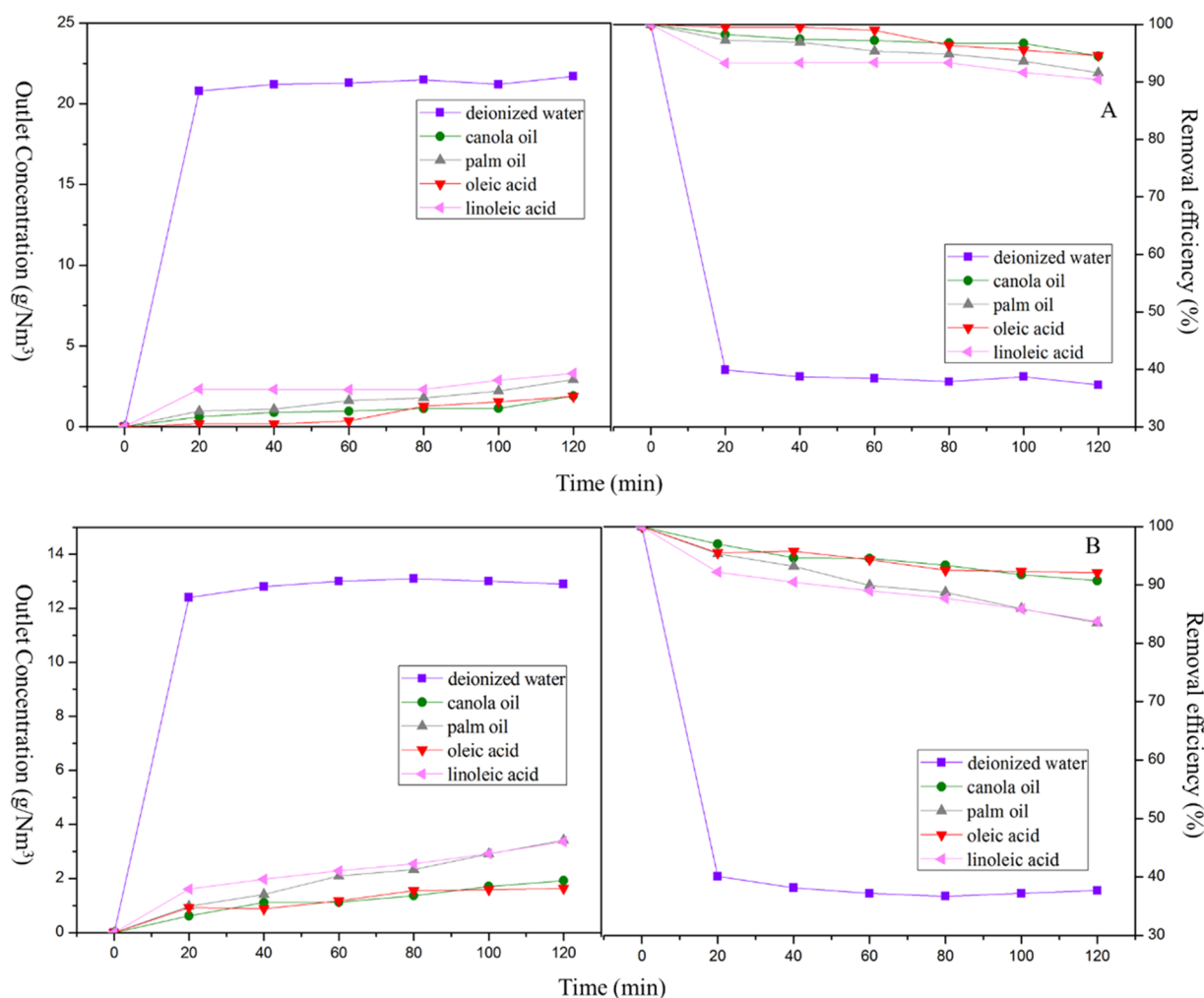
Figure 1. Model tar removal performance of different solvents (20 °C). A: removal of benzene; B: removal of toluene.
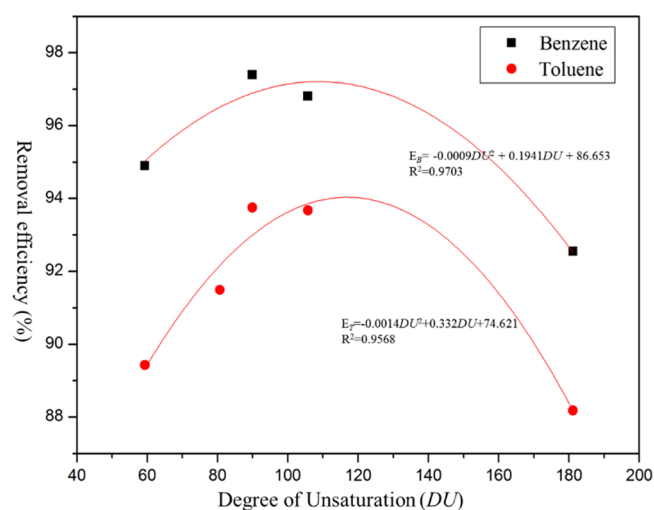

Figure 2. Effect of DU on the removal of benzene and toluene (20 °C).

absorption. However, further elevating DU by increasing poly-unsaturated fatty acids exerted negative effects. Because poly-unsaturated fatty acids have the bended structure and tend to be more polar, they decreased the absorption capacity of tar. It further revealed that the mono-unsaturated fatty acid, which

can be represented by oleic acid, was considered as the active compound responsible for tar absorption. A similar phenomenon was also found by Verkempinck et al.[37] who clarified that mono-unsaturated fatty acids were more hydrophobic compared to poly-unsaturated fatty acids when carotenoids were dissolved in oil emulsions.

2.2.2. Effects of ACL and AMW. The effects of ACL and AMW of different solvents on benzene and toluene removal are presented in Figure S2. It should be noted that oleic acid has the same ACL as linoleic acid, and Figure S2A is drawn based on the data of oleic acid, while linoleic acid's situation can be found in Figure S3. According to Figure S3, it can be observed that ACL posed a significant influence on model tar removal: the longer chain the solvent has, the better the removal it could achieve. This might be explained from two aspects: on the one hand, the longer chain brought the lower polarity, thus favoring "like dissolves like" absorption of tars. On the other hand, high-ACL fatty acids tended to have high molecular weights, and the bigger molecular weight could enhance van der Waals forces thus improving the absorption. This could also be confirmed by Figure S2B. However, linoleic acid which has high ACL and AMW, cannot provide better removal performance, which may be influenced by the polarity. Hence, it led to a failed fitting in Figure S2B.

2.2.3. Effects of Absorption Temperature and Kinetic Viscosity (KV). The biomass syngas coming out of the gasifier is

typically at high temperature, which is approximately 400 to 600 °C for downdraft fixed-bed gasifiers and approximately 150 °C for updraft fixed-bed gasifiers. Therefore, cooling and condensation is efficient for removal of gravimetric tar. Moreover, temperature strongly affected the cooling effect and KV of oils, hence exerting obvious influence on the absorption of model tar compounds. The effects of temperature on removal of benzene, toluene, and phenol by different solvents are plotted in Figure 3, and the potential effects of KV
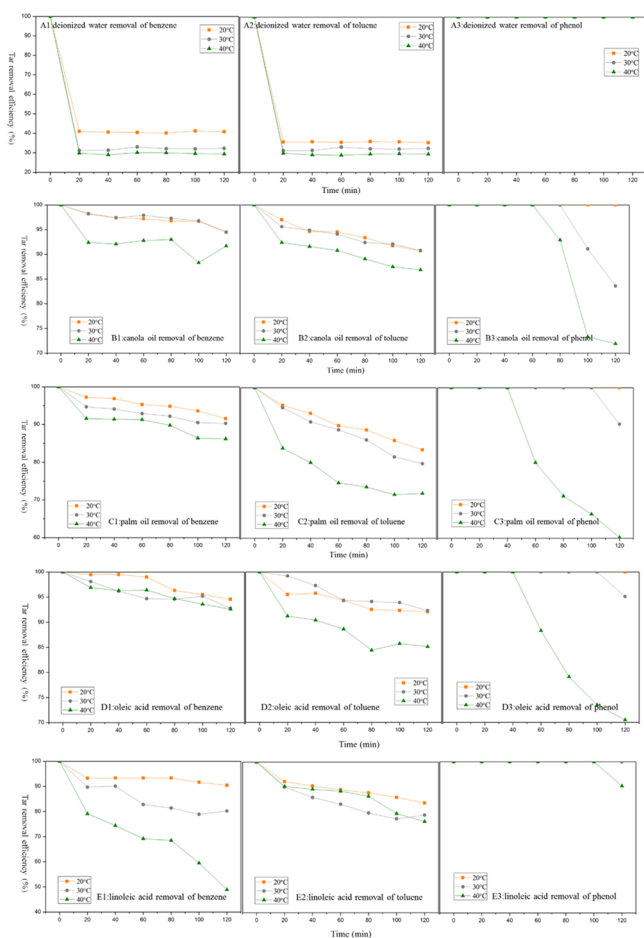

Figure 3. Effects of temperature on the absorption of different model tar compounds (A1, A2, and A3 corresponding to deionized water removal of benzene, toluene, and phenol, respectively; B1, B2, and B3 corresponding to canola oil removal of benzene, toluene, and phenol, respectively; C1, C2, and C3 corresponding to palm oil removal of benzene, toluene, and phenol, respectively; D1, D2, and D3 corresponding to oleic acid removal of benzene, toluene, and phenol, respectively; and E1, E2, and E3 corresponding to linoleic acid removal of benzene, toluene, and phenol, respectively).

at 40 °C is also presented in Figure S4. It can be found from Figure 3 A1, A2, and A3 that deionized water had relative poor capacity for the absorption of nonpolar tar. The removal efficiencies of benzene and toluene were lower than 40%, and they decreased with the increase of the temperature. It implied that the dominant function of deionized water is condensation during removal of benzene and toluene; thus, the lower temperature brought better performance. Additionally, the absorption of phenol by deionized water was very stable at 100%, which indicated the sufficient capacity for phenol absorption at a certain tar load and temperature range.

For the other four oily solvents, generally, increasing absorption temperature caused the decline of the removal efficiency. It could be explained from two aspects: on one hand, the higher temperature was not favorable for tar cooling and condensation. On the other hand, higher temperature could weaken the van der Waals forces, which is also harmful for tar removal. Oleic acid showed the best performance on benzene and toluene removal, and the efficiency could be maintained at approximately 95 and 85%, respectively, while the increasing temperature only slight decreased the efficiency. However, regarding phenol removal, linoleic acid might be the better choice. Phenol could be thoroughly removed by linoleic acid in most of tests, and there was only a slight decrease when the temperature was at 40 °C. The superior performance was probably due to its stronger polarity.

It has been reported by Nakamura et al.,[22] who used bio-oil for tar absorption, that the higher temperature could reduce the KV of bio-oil and increase the contact area between gas and solvents, thus improving the removal efficiency. However, this phenomenon was not observed in our experiments. As depicted in Figure S4, the influence of KV on tar absorptions is complex. As for phenol, it obeyed the fact that a lower KV means better removal. While the removal efficiency of benzene and toluene could not build an obvious relationship with KV. We can elaborate that, with a relative low test temperature in 20 to 40 °C, polar dissolution and physical absorption dominated more in benzene and toluene removal. However, in the situation of phenol, the condensation effect was more important.

2.3. Grey Relational Analysis. Grey relational analysis is an applicable tool for solving multiple-attribute decision-making problems.[38] According to the above, the DU, ACL, AMW, and temperature all can affect the absorption process, and therefore, the Grey relational analysis is used for determining and comparing their significance on the removal of benzene, toluene, and phenol.

Grey relational analysis consists of four steps, including initial zeroing, the calculation of the absolute relevance coefficients, the calculation of the relative relevance coefficients, and the calculation of the comprehensive relevance coefficients. Based on the comparison of comprehensive relevance coefficients of each factor, the importance can be evaluated. The process of Grey relational analysis of DU and temperature on benzene removal is displayed here, and other data for Grey relational calculations can be found in the Supporting Information. The experimental data are summarized and listed in Table 3. First, two kinds of initial zeroing procedures are conducted as difference zeroing and ration zeroing, and they can be expressed as eqs 1 and 6.

$$X_r^0 = [(x_{r,1} - x_{r,1}), (x_{r,2} - x_{r,1}), (x_{r,3} - x_{r,1}), ..., (x_{r,12} - x_{r,1})]$$

$$= [x_{r,1}^0, x_{r,2}^0, x_{r,3}^0, ..., x_{r,12}^0] = [96.8 - 96.8, 94.96 - 96.8, 97.3 - 96.8,$$

$$..., 66.6 - 96.8] = [0, -1.9, 0.59, -4.25, 0.22, -4.35, -1.53, -12.95,$$

$$-5.09, -7.35, -1.72, -30.2] \tag{1}$$

$$X_{DU}^0 = [(x_{DU,1} - x_{DU,1}), (x_{DU,2} - x_{DU,1}), (x_{DU,3} - x_{DU,1}),$$

$$..., (x_{DU,12} - x_{DU,1})] = [x_{DU,1}^0, x_{DU,2}^0, x_{DU,3}^0, ..., x_{DU,12}^0]$$

$$= [105.75 - 105.75, 59.32 - 105.75, 89.92 - 105.75, ..., 181.13 - 105.75]$$

$$= [0, -46.43, -15.83, 75.88, 0, -46.43, -15.83, 75.38, 0, -46.43,$$

$$-15.83, 75.38] \tag{2}$$

Table 3. Data of Factors DU and Temperature on the Average Removal Efficiency of Benzene[a]

variables	DU on the absorption of benzene				
	1	2	3	4	5
$x_{r,\,i}$	96.8	94.9	97.39	92.55	97.02
$x_{DU,\,i}$	105.75	59.32	89.92	181.13	105.75
$x_{T,\,i}$	20	20	20	20	30
	6	7	8	9	10
$x_{r,\,i}$	92.45	95.27	83.85	91.71	89.45
$x_{DU,\,i}$	59.32	89.92	181.13	105.75	59.32
$x_{T,\,i}$	30	30	30	40	40
	11	12			
$x_{r,\,i}$	95.08	66.6			
$x_{DU,\,i}$	89.92	181.13			
$x_{T,\,i}$	40	40			

[a]Where $x_{r,\,i}$, $x_{DU,\,i}$, and $x_{T,\,i}$ are the experimental results as the removal efficiency, DU value, and corresponding temperature in group i, respectively.

$$X_T^0 = [(x_{T,1} - x_{T,1}),\ (x_{T,2} - x_{T,1}),\ (x_{T,3} - x_{T,1}),$$
$$..., (x_{T,12} - x_{T,1}) = [x_{T,1}^{\ 0},\ x_{T,2}^{\ 0},\ x_{T,3}^{\ 0},\ ...,\ x_{T,12}^{\ 0}]$$
$$= [20-20,\ 20-20,\ 20-20,\ ...,\ 40-20]$$
$$= [0, 0, 0, 0, 10, 10, 10, 10, 20, 20, 20, 20] \tag{3}$$

$$X_r^{0\prime} = \left[\frac{x_{r,1}}{x_{r,1}},\ \frac{x_{r,2}}{x_{r,1}},\ \frac{x_{r,3}}{x_{r,1}},\ ...\ \frac{x_{r,12}}{x_{r,1}} \right] = [x_{r,1}^{\ 0\prime},\ x_{r,2}^{\ 0\prime},\ x_{r,3}^{\ 0\prime},\ ...x_{r,12}^{\ 0\prime}]$$
$$= [1, 0.980, 1.006, 0.956, 1.002, 0.955, 0.984, 0.866, 0.947, 0.924,$$
$$0.982, 0.688] \tag{4}$$

$$X_{DU}^{0\prime} = \left[\frac{x_{DU,1}}{x_{DU,1}},\ \frac{x_{DU,2}}{x_{DU,1}},\ \frac{x_{DU,3}}{x_{DU,1}},\ ...,\ \frac{x_{DU,12}}{x_{DU,1}} \right] = [x_{DU,1}^{\ 0\prime}$$
$$,\ x_{DU,2}^{\ 0\prime},\ x_{DU,3}^{\ 0\prime},\ ...,\ x_{DU,12}^{\ 0\prime}] = [1, 0.561, 0.850, 1.713, 1, 0.561, 0.850$$
$$, 1.713, 1, 0.561,\ 0.850,\ 1.713] \tag{5}$$

$$X_T^{0\prime} = \left[\frac{x_{T,1}}{x_{T,1}},\ \frac{x_{T,2}}{x_{T,1}},\ \frac{x_{T,3}}{x_{T,1}},\ ...,\ \frac{x_{T,12}}{x_{T,1}} \right] = [x_{T,1}^{\ 0\prime},\ x_{T,2}^{\ 0\prime},\ x_{T,3}^{\ 0\prime},\ ...,\ x_{T,12}^{\ 0\prime}]$$
$$= [1, 1, 1, 1, 1.5, 1.5, 1.5, 1.5, 2, 2, 2, 2] \tag{6}$$

where X_r^0, X_{DU}^0, and X_T^0 represent the absolute relevance sequences of the removal efficiency, DU, and temperature based on the difference initial zeroing, while $X_r^{0\prime}$, $X_{DU}^{0}{}^{\prime}$, and $X_T^{0\prime}$ represent the absolute relevance sequences of the removal efficiency, DU, and temperature based on the ratio initial zeroing.

Then, the absolute relevance coefficients of DU and temperature can be obtained by following:

$$\varepsilon_{r,DU} = \frac{1 + |s_r| + |s_{DU}|}{1 + |s_r| + |s_{DU}| + |s_r - s_{DU}|} \tag{7}$$

$$\varepsilon_{r,T} = \frac{1 + |s_r| + |s_T|}{1 + |s_r| + |s_T| + |s_r - s_T|} \tag{8}$$

where $|s_r|$, $|s_{DU}|$, and $|s_T|$ are the difference absolute relevance values between the removal efficiencies, DU values, and temperatures, respectively, and they can be calculated by eqs 9 to 11.

$$|s_r| = \left| x_{r,2}^{\ 0} + x_{r,3}^{\ 0} + x_{r,4}^{\ 0} + ... + x_{r,11}^{\ 0} + \frac{1}{2}x_{r,12}^{\ 0} \right| \tag{9}$$

$$|s_{DU}| = \left| x_{DU,2}^{\ 0} + x_{DU,3}^{\ 0} + x_{DU,4}^{\ 0} + ... + x_{DU,11}^{\ 0} \right.$$
$$\left. + \frac{1}{2}x_{DU,12}^{\ 0} \right| \tag{10}$$

$$|s_T| = \left| x_{T,2}^{\ 0} + x_{T,3}^{\ 0} + x_{T,4}^{\ 0} + ... + x_{T,11}^{\ 0} + \frac{1}{2}x_{T,12}^{\ 0} \right| \tag{11}$$

Thus, $\varepsilon_{r,\,DU}$ and $\varepsilon_{r,\,T}$ can be obtained as 0.50450 and 0.50153, respectively.

The third step is the calculation of the relative relevance coefficient, which can be expressed by eqs 12 and 13.

$$\gamma_{r,DU} = \frac{1 + |s_r{}^\prime| + |s_{DU}{}^\prime|}{1 + |s_r{}^\prime| + |s_{DU}{}^\prime| + |s_r{}^\prime - s_{DU}{}^\prime|} \tag{12}$$

$$\gamma_{r,T} = \frac{1 + |s_r{}^\prime| + |s_T{}^\prime|}{1 + |s_r{}^\prime| + |s_T{}^\prime| + |s^\prime - s_T{}^\prime|} \tag{13}$$

where $|s_r{}^\prime|$, $|s_{DU}{}^\prime|$, and $|s_T{}^\prime|$ are the ratio absolute relevance values between the removal efficiencies, DU values, and temperatures, respectively, and they can be obtained by eqs 14 to 16.

$$|s_r{}^\prime| = \left| x_{r,2}^{\ 0\prime} + x_{r,3}^{\ 0\prime} + x_{r,4}^{\ 0\prime} + ... + x_{r,11}^{\ 0\prime} + \frac{1}{2}x_{r,12}^{\ 0\prime} \right| \tag{14}$$

$$|s_{DU}{}^\prime| = \left| x_{DU,2}^{\ 0\prime} + x_{DU,3}^{\ 0\prime} + x_{DU,4}^{\ 0\prime} + ... + x_{DU,11}^{\ 0\prime} \right.$$
$$\left. + \frac{1}{2}x_{DU,12}^{\ 0\prime} \right| \tag{15}$$

$$|s_T{}^\prime| = \left| x_{T,2}^{\ 0\prime} + x_{T,3}^{\ 0\prime} + x_{T,4}^{\ 0\prime} + ... + x_{T,11}^{\ 0\prime} + \frac{1}{2}x_{T,12}^{\ 0\prime} \right| \tag{16}$$

Thus, $\gamma_{r,\,DU}$ and $\gamma_{r,\,T}$ can be calculated as 0.9742 and 0.8166, respectively.

Finally, the comprehensive relevance coefficients are calculated by eqs 17 and 18.

$$\rho_{r,DU} = \theta\varepsilon_{r,DU} + (1 - \theta)\gamma_{r,DU} \tag{17}$$

$$\rho_{r,T} = \theta\varepsilon_{r,T} + (1 - \theta)\gamma_{r,T} \tag{18}$$

Herein, the index for distinguishability as θ is set at 0.5.

Therefore, the final results of comprehensive relevance coefficients are obtained as 0.7394 and 0.6591 for DU and temperature on the benzene removal efficiencies, respectively. Grey relational analyses of other factors and model tar compounds are the same as above, and all the results are listed in Table 4.

It could be concluded from Table 4 that, generally, AMW and ACL showed more prominent influence during model tar absorption. AMW was the most important factor for removing all kinds of tested tars due to it strongly affecting the van der Waals forces. This result was also in good agreement with the conclusions in Section 2.2.2, and it demonstrated that, in the relatively low-temperature range, the absorption could be improved by enhancing van der Waals forces. Meanwhile, DU exerted less significance on the absorption mainly because it could not directly reflect the polar absorption capacity of oils. Based on the aforementioned discussion, it might be the

Table 4. Results of Grey Relational Analysis

parameters	benzene removal	toluene removal	phenol removal
DU	0.7394	0.7384	0.7395
AMW	0.9810	0.7669	0.7739
ACL-1[a]	0.7759	0.7603	0.7397
ACL-2[a]	0.7425	0.7471	0.7448
temperature	0.6591	0.6584	0.6592

[a]The data of ACL-1 and ACL-2 are calculated with oleic acid and linoleic acid, respectively, due to the fact that they have the same average chain length.

content of mono-unsaturated fatty acids that had the significant influence on polarity instead of DU. For temperature, it showed the lowest influence probably due to the relatively low experimental range in the present study, but it is still curial for maintaining the tar absorption capacity, especially for phenol removal.

3. PERSPECTIVE AND FUTURE DIRECTIONS

Vegetable oil absorption for tar removal is an efficient and low-cost method, and through a better understanding of the oils' properties and their effects, we may find a way to improve the performance. Some perspective and future directions can be drawn based on the results above.

(1) A high concentration of mono-unsaturated fatty acids and high content of heavy and long-chain molecules are favorable for tar absorption. Therefore, it is meaningful for modulating oil-based scrubber media by extracting such eligible fatty acid compounds from the cheaper sources, for example, waste cooking oil. Further attention might be given on the in-depth mechanism of tar absorption

(2) Vegetable oils, especially oleic acid-enriched oils, have excellent tar absorption capacity as well as stable removal performance. They make the oil-based scrubber a potential alternative for second-stage tar treatment. With the coupling of cyclone or water cooling towers, the oil-based scrubber can play an important role for trapping the light tars, which are not thoroughly condensed in the primary units.

(3) Tar may not be regarded as pollution; it can also be considered as a mixture of some valued chemicals. Thus, the separation and purification of the collected tar may be more meaningful and power-saving than directly cracking it. It was elaborated that different model tars have different responses for solvents; therefore, it might be interesting to magnify these effects by modulating specific solvents to obtain useful high-purity chemical feedstock from tar.

4. CONCLUSIONS

Deionized water, canola oil, palm oil, pure oleic acid, and linoleic acid were employed as solvents for absorption of different model tar compounds. Oleic acid showed the best performance, and the 2 h average removal efficiency could reach 97.39, 93.75, and 100% for benzene, toluene, and phenol, respectively, at 20 °C. The composition and properties of solvents affected the absorption performance, and the mono-unsaturated fatty acid, heavy molecular weight, and long chain length all enhanced the tar removal. Grey relational analysis was conducted to figure out the influence of each factor on tar removal, and the average molecular weight had the most significance in that the comprehensive relevance coefficients reached 0.9810, 0.7669, and 0.7739 for benzene, toluene, and phenol, respectively. Therefore, it is believed that, at lower temperature, molecular weight plays a more important role, and the absorption can be strongly improved by enhancing van der Waals forces.

5. EXPERIMENTAL SETUP

5.1. Solvents and Chemicals. In total, five solvents were selected for tar absorption, including deionized water, canola oil, palm oil, oleic acid, and linoleic acid. Canola oil and palm oil were purchased commercially from a retailer in Tianjin, north of China. Oleic acid and linoleic acid (AR, purity of 99%) were purchased from Aladdin Biochemical Technology Co. Ltd., in Shanghai, China. The pictures of the oils are presented in Figure S1.

Tar can be variable by different biomass feedstock and different types of gasifiers; hence, it is reasonable to investigate tar removal using model tar compounds. Toluene (C_7H_8, analytical grade, Jiangtian Chemical Co., Ltd., Tianjin, China)
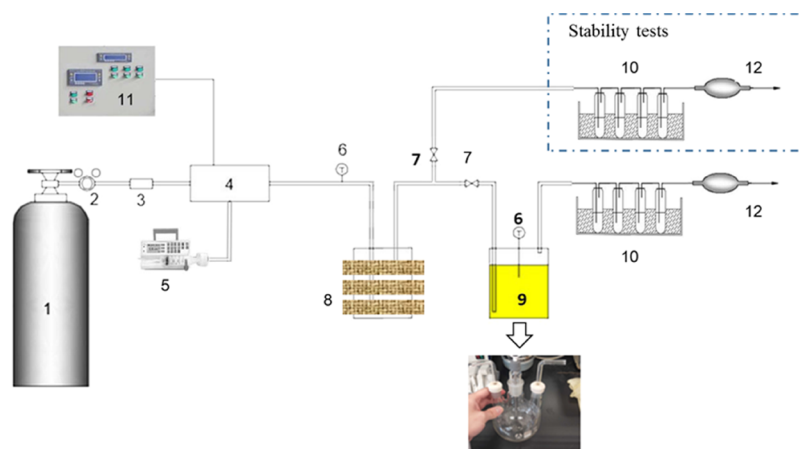

Figure 4. Schematic diagram of the experimental apparatus. (1) Gas cylinder, (2) on−off valve, (3) gas meter, (4) evaporator, (5) syringe pump, (6) K-type thermocouple, (7) valve, (8) mixing chamber (covered by heating tapes), (9) Wouff's glass bottle with solvents, (10) tar sampling and measurement unit, (11) temperature control panel, and (12) gas collection and release.

was selected as a model tar because it makes up the largest proportion in typical tar, which can be higher than 20 wt %.[39] Based on conclusions of Bhoi et al.,[40] benzene is the hardest part to remove by vegetable oils, so benzene (C_6H_6, analytical grade, Jiangtian Chemical Co., Ltd., Tianjin, China) was also taken as model tar. Moreover, phenol (C_6H_6O, analytical grade, Jiangtian Chemical Co., Ltd., Tianjin, China) as a representative of a polar tar compound[18] was also investigated. In addition, IPA (isopropanol, chromatographically pure grade, Jiangtian Chemical Co., Ltd., Tianjin, China)[41] was employed for tar measurement following the tar protocol.[42]

5.2. Experiments. The experimental procedure is depicted in Figure 4. N_2 was used as a carrier and purge gas with a flow rate of 200 mL/min. Benzene, toluene, and phenol were premixed by the ratio of 50:30:20 (wt %). Then, the mixed tar compounds were heated in the evaporator whose temperature was kept at 250 °C. When the tar stream became stable, it passed through the mixing chamber and went into the Wouff's bottle (500 and 400 mL solvents in it) for absorption tests. The temperature of solvent was monitored and controlled from 20 to 40 °C. After absorption, all the evolving gas was washed by IPA in the tar sampling and measurement unit. Four bottles with 250 mL of IPA in each were connected and placed in a cold trap (0 ± 1 °C). The concentrations of model tar compounds in IPA were measured by gas chromatography−mass spectrometry with external standard methods (GC−MS, Rtx-5MS as a 30.0 m capillary column, 0.25 mm in inner diameter and 0.25 μm in film thickness). Each absorption test lasted for 120 min, and the evolved gas was sampled and analyzed every 20 min. It should be noted that, the initial inlet concentrations of model tars (stable condition) were obtained by directly connecting the mixing chamber with the IPA unit, and the corresponding values of benzene at 34.6 g/Nm³, toluene at 20.7 g/Nm³, phenol at 13.8 g/Nm³ were stabilized and set as background.

5.3. Data Statistical Analysis. The model tar removal efficiency in a single sampling point is defined by the following format

$$X_{T,i} (\%) = \frac{\text{amount of tar input} - \text{amount of tar outlet (trapped by IPA)}}{\text{amount of tar input}} \times 100 \tag{19}$$

where T represents benzene, toluene, and phenol and i indicates the number of sampling points in each run.

The average tar removal efficiency in the whole trial is defined as

$$\overline{X}_T (\%) = \frac{\sum_{i=1}^{6} X_{T,i}}{6} \tag{20}$$

The average unsaturation degree of the fatty acid could be expressed by the iodine number (IN).[43] It indicates the mass of iodine needed to completely saturate the certain amount of give oils by means of a stoichiometric reaction. The calculation method is presented in eq 21.

$$DU = IN = \sum \left[\frac{(254 \times D \times A_i)}{M_{w_i}} \right] \tag{21}$$

where A_i is the percentage composition of each fatty acid in oils, D is the number of double bonds present in each unsaturated fatty acid, and M_{w_i} is the molecular weight of each fatty acid.

The average chain length (CL) is defined by eq 22 as the following:

$$ACL = \sum [L_{C_i} \times A_i] \tag{22}$$

where L_{C_i} is the chain length of each fatty acid detected in oils.

The average molecule weight (AMW) is defined by eq 23 as following

$$AMW = \sum [M_{C_i} \times A_i] \tag{23}$$

where M_{C_i} is the molecule weight of each fatty acid detected in oils.

All the experiments were carried out in triplicate, and the results were displayed and plotted by the mean value.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02050.

Table S1: data of factors on the average removal efficiency of benzene, toluene, and phenol, Figure S1: pictures of absorption media (canola oil, palm oil, oleic acid, and linoleic acid), Figure S2: effects of ACL and AMW on the removal of benzene and toluene (20 °C), Figure S3: effect of the average chain length on the tar removal (canola oil, palm oil, and linoleic acid), and Figure S4: effects of KV on the average removal efficiency of benzene, toluene, and phenol (40 °C) (PDF)

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Notes

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